Supporting Information for

Simultaneous topographic and chemical patterning via imprinting defined nano-reactors

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1. Feasibility: Morphology and Feature Size (PVP-PS)

We studied the feasibility and replication fidelity along with the patterning quality of the double imprinting method by using a series of line- and square-arrays whose feature sizes ranged from 20 nm to 100 nm (Figure. S1). The spacing between features were always equal to the feature width and all features were 80 nm deep. The polymer blends being tested were polyvinylpyridine (PVP, Mw=120 kg/mol, T_g =127 ℃) and polystyrene (PS, Mw=125-250 kg/mol, T_g= 105 ℃). A 110 nm thick PVP film was spincoated on a Si substrate and imprinted by a Si mold at 170 ℃. Subsequently, a 100 nm thick PS film which was spin coated onto Si substrate was imprinted by the patterned PVP film at 130 ℃. In order to check the morphology of each layer after double imprinting, either the PS or PVP film was selectively dissolved by cyclohexane or ethanol, respectively.

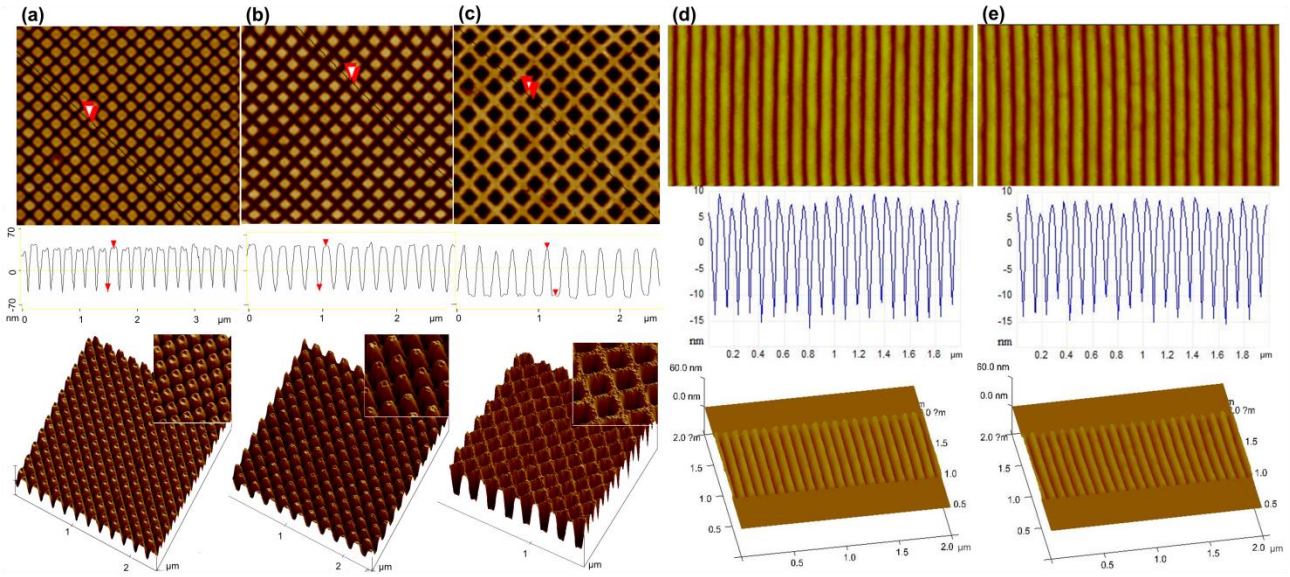

Figure S1. AFM images of patterned PVP film (a), (d) before and (b), (e) after imprinting PS film and (c), (f) PS film imprinted by PVP. Feature size: 100 nm wide squares with 100 nm spacing. (a), (b), (c): topological and cross-sectional images of the polymer patterns; (d), (e), (f): 3D AFM images. Insets: Magnified image of the 3D patterns. Image (g)-(j) are AFM images and cross-sectional profiles of 20-nm-wide line patterns in PVP film imprinted by Si mold (g, i) and the replicated lines pattern in PS film imprinted by pre-patterned PVP film (h, j). Image (i) and (j) are three-dimension images of the same samples in (g) and (h), respectively.

Figure S1a-S1f show AFM images of a PVP film before (a, d) and after (b, e) imprinting a PS film (c, f) with 100 nm wide dots. Figure S1a and S1b clearly show that the height and width of the features in the PVP film do not change measurably during the imprinting of the PS layer and subsequent exposure to cyclohexane for the removal of PS layer. The patterns obtained in the PS films were the exact replicates of the dot array in the PVP film, with exactly the same width of 100 nm and the same depth of 84-87 nm as the dots in PVP. The double imprinting was able to transfer features down to 20 nm in size, as shown in Figure S1g-S1j in which uniform 20 nm wide line arrays were obtained in PVP and PS layers. The insets to the 3D AFM images show a tiny "dimple"

structure for the PVP pillars. This is a well-known artifact seen during nanoimprinting of features due to the capillary force induced deformation.[1]

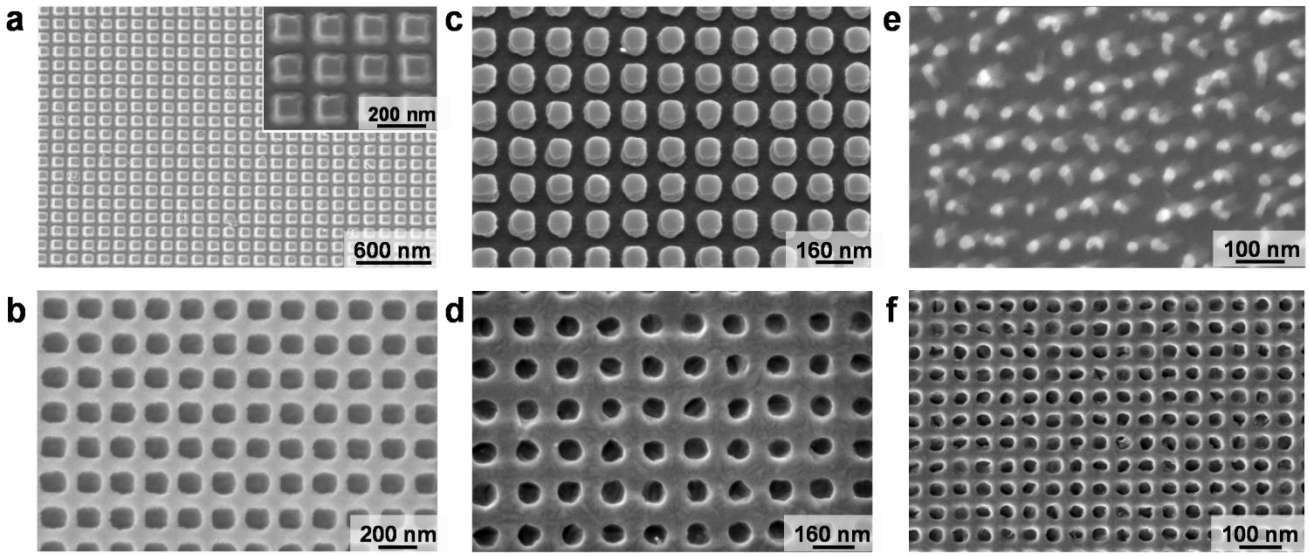

Figure S2. SEM images of (a), (c), (e) pillar arrays in PVP films after imprinting PS films and (b), (d), (f) hole arrays in PS films imprinted by prepatterned PVP film. Pillar width: (a), (b) 100 nm, (c), (d) 80 nm, (e), (f) 25 nm. Inset in (a): magnified image of the pillar array.

The SEM images in Figure S2 show 100-, 80- and 25-nm PVP pillar arrays after imprinting PS films and the PS films imprinted by PVP molds. All the samples were washed by solvents prior to imaging to remove unwanted residue. The very uniform and regular hole arrays in the PS film (Figure S2b, S2d and S2f) were the exact negative replica of the pillar arrays in the PVP film. This perfect match showed the reliability of our approach to transfer topological patterns from the original mold. The smallest PVP pillars showed some bending/distortion in the AFM image (Figure S2e), which was due to the mechanical instability during the solvent wash. Indeed, they were still able to imprint the PS film and precisely transfer their patterns (Figure S2f).

2. Immiscible/miscible polymer pairs (PS/PEO and PMMA/PEO)

The double imprinting process only required that the two polymers had a difference in T_g (the smallest difference tested in this work was 20 ℃). It was therefore possible to create nanoscale patterns in both miscible and immiscible polymer blends. Here, we compared patterns formed in the immiscible polymer pair PS/polyethylene oxide (PEO, Mw=100 kg/mol, *MP*=60 ℃) and miscible pair polymethyl methacrylate (PMMA, Mw=120 kg/mol, T_g =99 ℃)/PEO.

First, PS and PMMA films were identically patterned at 160 ℃ under 20 bar for 300 seconds by an ETFE mold. Subsequently, PEO was imprinted by PS or PMMA at 85 ℃ under 20 bar pressure for 300 seconds. To check the morphology of the PS film after imprinting PEO, the polymer bilayer was soaked in ethanol for 30 minutes followed by ultrasonication for 5 minutes to remove PEO. Alternatively, the PS could be selectively removed by cyclohexane to expose the PEO layer. Figure S3 shows the excellent quality of the matching patterns in PS and PEO. The PMMA/PEO blend could be easily separated after imprinting by applying mechanical force. While nano-features were created in both immiscible and miscible polymer pairs, the uneven surface on the PMMA and PEO surfaces seen in the AFM images (Figure S3c and S3d) indicated that polymers at the interface started to diffuse into the opposite layer. Therefore, diffusion across the interface of miscible polymer pairs during imprinting should be controlled by adjusting imprinting time and temperature for high precision patterning.

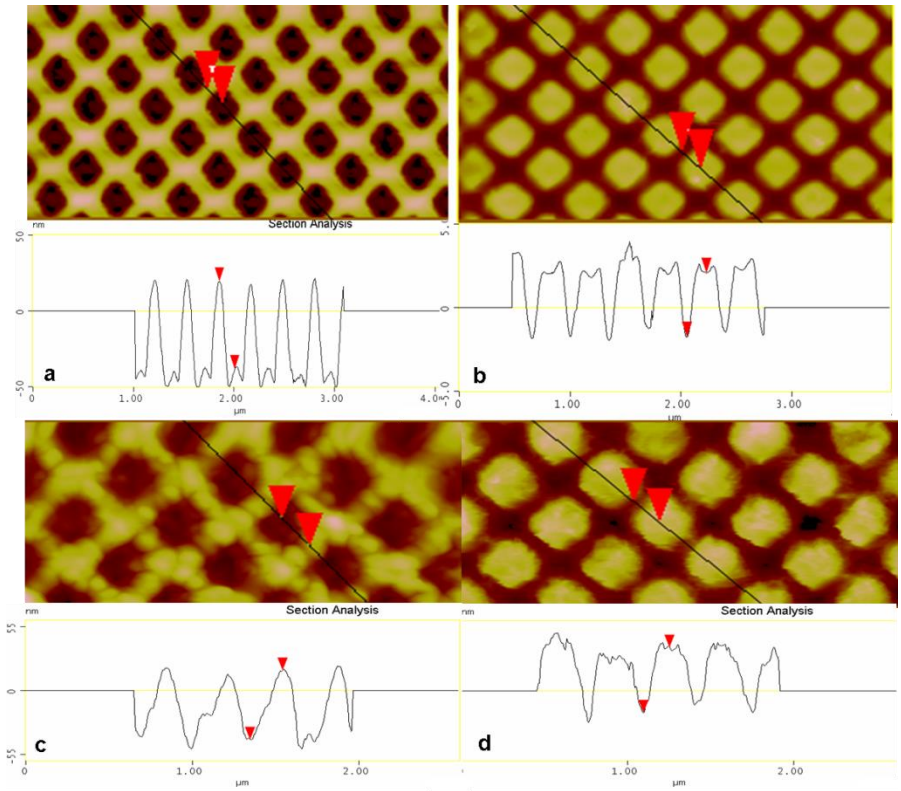

Figure S3. Topological and cross-sectional AFM images of 175 nm wide square hole arrays (100 nm space) in (a) PS and (c) PMMA films imprinted by an ETFE mold. (b), (d) are topological and cross-sectional AFM images of PEO films imprinted by pre-patterned PMMA film (b) and PS film (d), respectively.

3. Total interface area in square patterns

The polymer mold was uniformly patterned with square pillars of width *l* and height *h*, whose period is *P*. The minimum repeating unit was indicated by the dashed square. Assuming the total patterned area is *A*, then the number of square pillar (N) contained in this area is:

$$N = A/P^2$$

The interface area of an individual pillar equals to the summation of its top area and side area, which is:

$$l^2 + 4l \times h$$

Therefore, the total interface area (A_i) found in a mold of area *A* equals to:

$$A_i = A/P^2 \times (l^2 + 4l \times h)$$

In our experiment, $P = 2l$. The above equation can be simplified as:

$$A_i = A/4 + Ah/l$$

It can be seen that the interface area is proportional to the aspect ratio of the square pillars, which is defined as h/l. When the reaction rate is a constant per unit surface area, the amount of final product will be determined by the aspect ratio.

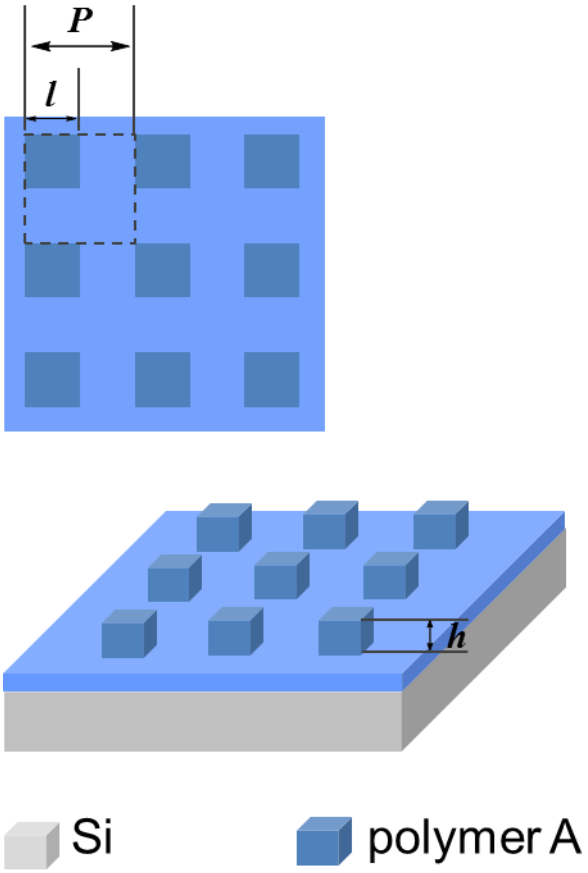

Figure S4. The top view (top) and 3D view (bottom) image of the square patterns used in imprinting. The geometric parameters of the patterns are labelled.

References

1 H. D. Rowland, A. C. Sun, P. R. Schunk, W. P. King, *Journal of Micromechanics and Microengineering*, 2005, **15**, 2414-2425.